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Description

The present invention relates to a stabilizing agent for aqueous enzyme-containing compositions. It is well-known that enzymes, when included in aqueous media, often tend to lose their activity on storage over longer periods. This is particularly so when the aqueous media contain other ingredients as well, which may accelerate the deactivation of enzymes. Such is for instance often the case if the aqueous media are aqueous liquid detergent compositions.

In the prior art numerous proposals have been made concerning enzyme stabilizers in aqueous enzyme-containing liquid detergent compositions. Such enzyme-stabilizing systems often comprise a polyol, such as glycerol or sorbitol. Recently were have proposed as enzyme-stabilizing system a mixture of a polyol and a boron compound in our Dutch patent application No. 7711925, laid open to public inspection on 3 May 1978.

Another proposal is made in UK Patent Specification Nr 2,021,142 (Economics Laboratories Inc.) to use a mixture of a polyol and a sulphur-containing anti-oxidant salt as enzyme-stabilizing mixture.

We have now found that the use of certain dicarboxylic acids instead of the polyol in the above systems equally provides for an enzyme-stabilisation effect. In some instances this effect is even superior to that which is obtained with the polyol-containing systems.

The present invention therefore relates to an aqueous, enzymatic liquid detergent composition comprising, in an aqueous medium an active detergent material, a detergent builder, enzymes and an enzyme-stabilizing system which contains a component (a) comprising boric acid, boric oxide or an alkali metal borate, and/or a reducing alkali metal salt having an oxygenated sulphur anion, S_aO_b , in which a and b are whole numbers from 1 to 8, characterized in that the enzyme-stabilizing system further comprises from 0.5—15% by weight of a component (b) selected from a dicarboxylic acid of the formula $COOH—(CHOH)_a—(CH_2)_b—(CHOH)_c—(CH_2)_d—COOH$, wherein a, b, c and d are whole numbers from 0—4, and the sum of a, b, c and d is from 0 to 4 maleic or fumaric acid as well as the alkali metal, ammonium, alkanolamine or alkaline earth metal salts thereof, or the anhydrides thereof.

Typical examples of alkali metal borates are sodium and potassium, ortho-, pyro- and meta-borates, -polyborates, and borax. Borax is the preferred alkali metal borate.

If component (a) comprises, or consists of, boric acid, boric oxide, or an alkali metal borate, the amount thereof ranges preferably from 1 to 15, more preferably from 3 to 10% by weight of the final aqueous enzyme-containing composition.

Component (a) also comprises, or consists of, a reducing alkali metal salt having an oxygenated sulphur anion S_aO_b in which a and b are whole numbers from 1 to 8. Typical examples of such reducing salts (which have an anti-oxidant effect) are sodium and potassium sulphites, -bisulphites, -metabisulphites and -thiosulphates. Sodium sulphite is the preferred reducing alkali metal salt.

If component (a) comprises, or consists of, the reducing alkali metal salt, the amount thereof ranges preferably from 2 to 20, more preferably from 5 to 15% by weight of the final aqueous, enzyme-containing composition.

Component (a) may also consist of mixtures of the various recited ingredients.

Component (b) consists of a dicarboxylic acid of the above general formula or mixtures of these acids; instead of the acids, the anhydrides can be used, or the alkali metal, ammonium, alkanolamine or alkaline earth metal salts of these acids. Typical examples of suitable dicarboxylic acids are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, tartaric acid, malic acid, tartaric acid, xylaric acid, arabimonic acid, glucaric acid, mucic acid and saccharic acid. In general, when $a:c = 0$, the dicarboxylic acids of the general formula with $b + d = 0—2$ are preferred over those with $b + d = 3—4$, and if $b + d = 0$, $a + c =$ preferably 4. When $a = c = 0$ and $b = d = 1$, the corresponding unsaturated dicarboxylic acid, viz maleic or fumaric acid, may also be used.

The amount of the acid(s) used ranges from 0.5—15, preferably from 2—10% by weight of the final aqueous enzyme-containing composition. Succinic acid or saccharic acid or the alkali metal or alkanolamine salts thereof are the preferred compounds, since they provide for an enzyme-stabilizing effect which is equal or superior to the effect obtained with the corresponding polyol-containing systems. As alkanolamine salts the mono-, di- or triethanolamine salts can be used as well as the corresponding isopropanol amine salts. The salts of the acids can also be formed in situ in the final composition by neutralization with the required base.

The preferred enzyme-stabilizing system according to the present invention comprises a mixture of sodium sulphite, borax and disodium succinate.

The aqueous liquid compositions in which the stabilizing systems of the invention are incorporated are aqueous, liquid enzymatic detergent compositions further comprising as essential ingredients enzymes, active detergents and a detergent builder.

The enzymes to be incorporated can be proteolytic, lypolytic, amylolytic and cellulolytic enzymes as well as mixtures thereof. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases. Although the liquid compositions of the present invention may have a near-neutral pH value, the present invention is

of particular benefit for enzymatic liquid detergents with a pH of 7.5 or above, especially those incorporating bacterial proteases of which the pH-optima lie in the range between 8.0 and 11.0, but it is to be understood that enzymes with a somewhat lower or higher pH-optimum can still be used in the compositions of the invention, benefiting from it.

5 Suitable examples of proteases are the subtilisins which are obtained from particular stains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase® (ex Gist-Brocades N.V., Delft, Holland) and Alcalase® (ex Novo Industri A/S, Copenhagen, Denmark).

As stated above, the present invention is of particular benefit for enzymatic liquid detergents incorporating enzymes with pH-activity and/or stability optima of above 8.0, such enzymes being 10 commonly called high-alkaline enzymes.

Particularly suitable are proteases obtained from strains of *Bacillus*, having maximum activity throughout the pH-range of 8—12, developed and sold by Novo Industri A/S under the registered trade name of Esperase® and Savinase®.

15 The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo.

High-alkaline amylases and cellulase can also be used, e.g. alpha-amylases obtained from a special strain of *B. licheniformis*, described in more detail in British Patent Specification No. 1,296,839 (Novo).

The enzymes can be incorporated in any suitable form, e.g. as a granulate (marumes, prills etc.), or as a liquid concentrate. The granulate form has often advantages.

20 The amount of enzymes present in the liquid composition may vary from 0.001 to 10% by weight, and preferably from 0.01 to 5% by weight.

The liquid detergent compositions of the invention furthermore comprise as essential ingredient an active detergent material, which may be an alkali metal or alkanol amine soap or a C₁₀—C₂₄ fatty acid, including polymerized fatty acids, or an anionic, nonionic, cationic, zwitterionic or amphoteric synthetic 25 detergent material, or mixtures of any of these.

Examples of anionic synthetic detergents are salts (including sodium, potassium, ammonium, and substituted ammonium salts, such as mono-, di- and triethanolamine salts) of C₉—C₂₀ alkylbenzene sulphonates, C₈—C₂₂ primary or secondary alkane sulphonates, C₈—C₂₄ olefin sulphonates, sulphonated polycarboxylic acids, prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, 30 e.g. as described in British Patent Specification Nr. 1,082,179, C₈—C₂₂ alkyl sulphates, C₈—C₂₄ alkyl-polyglycoether sulphates (containing up to 10 moles of ethylene oxide); further examples are described in "Surface Active Agents and Detergents" (Vol. I and II) by Schwartz, Perry and Berch.

35 Examples of nonionic synthetic detergents are the condensation products of ethylene oxide, propylene oxide and/or butyleneoxide with C₈—C₁₈ alkylphenols, C₈—C₁₈ primary or secondary aliphatic alcohols, C₈—C₁₈ fatty acid amides; further examples of nonionics include tertiary amine oxides with one C₈—C₁₈ alkyl chain and two C_{1—3} alkyl chains. The above reference also describes further examples of nonionics.

The average number of molecules of ethylene oxide and/or propylene oxide present in the above nonionics varies from 1—30; mixtures of various nonionics, including mixtures of nonionics with a lower and a higher degree of alkoxylation, may also be used.

40 Examples of cationic detergents are the quaternary ammonium compounds such as alkyldimethylammonium halogenides, but such cationics are less preferred for inclusion in enzymatic detergent compositions.

45 Examples of amphoteric or zwitterionic detergents are N-alkylamino acids, sulphobetaines, condensation products of fatty acids, with protein hydrolysates, but owing to their relatively high costs they are usually used in combination with an anionic or a nonionic detergent. Mixtures of the various types of active detergents may also be used, and preference is given to mixtures of an anionic and a nonionic detergent active. Soaps (in the form of their sodium, potassium, and substituted ammonium salts) or fatty acids may also be used, preferably in conjunction with an anionic and/or a nonionic synthetic detergent.

50 The amount of the active detergent material may vary from 1 to 60%, preferably from 2—40 and especially preferably from 5—25%; when mixtures of e.g. anionics and nonionics are used, the relative weight ratio varies from 10:1 to 1:10, preferably from 6:1 to 1:6. When a soap is also incorporated, the amount thereof is from 1—40% by weight.

55 The liquid compositions of the invention may further contain up to 60% of a suitable builder, such as sodium, potassium and ammonium or substituted ammonium pyro- and tripolyphosphates, -ethylene-diamine tetraacetates, -nitrilotriacetates, -etherpolycarboxylates, -citrates, -carbonates, -orthophosphates, zeolites, carboxymethyloxysuccinate, etc. Particularly preferred are the polyphosphate builder salts, nitrilotriacetates, citrates, zeolites, and mixtures thereof. In general the builders are present in an amount of 1—60, preferably 5—50%, and particularly preferably 5—30% by weight of the final composition.

60 The amount of water present in the detergent compositions of the invention may vary from 5 to 70% by weight.

65 Other conventional materials may also be present in the liquid detergent compositions of the invention, for example soil-suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, silicates, optical brighteners, suds depressants such as silicones, germicides, anti-tarnishing agents, opacifiers, fabric softening agents, oxygen-liberating bleaches such as hydrogen peroxide, sodium perborate or percarbonate, diperisophthalic anhydride, with or without bleach precursors, buffers and the like. When the

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compositions contains a builder, it may sometimes be advantageous to include a suspension stabilizer in the composition to provide a satisfactory phase-stability. Such stabilizers include natural or synthetic polymers.

5 Suitable examples of such suspension stabilizers are polyacrylates, copolymers of maleic anhydride and ethylene or vinylmethylene, and polymers of acrylic acid, cross-linked with not more than 10% of a vinyl-group containing cross-linking agent, e.g. polymers of acrylic acid, cross-linked with about 1% of a polyallyl ether of sucrose having an average of about 5.8 alkylgroups for each sucrose molecule. Examples of the latter are commercially available products, available under the registered trade name of Carbopol of B. F. Goodrich Co. Ltd.

10 In general, if a suspension stabilizer is required, it will be included in an amount of 0.1—2, usually 0.25—1% by weight of the final composition.

The invention will now be further illustrated by way of Example. In the examples, all the percentages are percentages by weight of the final composition.

15 The pH of the final composition is near neutral, preferably 7.5 or higher, and is, if necessary, buffered to a value within that range by addition of a suitable buffer system. The pH of the wash liquor, when using the composition, is about 1 pH unit higher than the above values at an in-use concentration of about 1%.

Example 1

The following composition was prepared:

		% by weight
20	Sodium dodecylbenzene sulphonate	5
25	C_{13} — C_{15} linear primary alcohol condensed with 7 moles of ethylene oxide, which is a mixture of ethylene and propylene oxide in a weight ratio of 92:8	2
30	Pentasodium triphosphate (anhydrous)	21
	Sodium carboxymethyl cellulose	0.2
35	Carbopol® 941 (a polymer of acrylic acid crosslinked with about 1% of a poly- alkylether of sucrose having an average of about 5.8 alkyl groups for each sucrose molecule)	0.4
40	Fluorescer	0.1
	Alcalase® marumes (activity 1.5 Anson unit/g)	0.7
45	Enzyme stabilizer or dicarboxylic acid	x
	Borax	y
50	Sodium sulphite (anhydrous)	z
	Water	to 100.0%
55	pH	7.5

x, y and z were varied, yielding a series of compositions 1—5.

60 The products were stored at 37°C and the residual enzymatic activity (RA) was determined at weekly intervals.

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The following results were obtained:

	<i>Composition 1:</i> x = 5%	Succinic acid	RA after
5	y = 3.5%		8 weeks:
	z = 8.0%		100%

10 The same composition, but with 5% glycerol instead of succinic acid, had an RA after 8 weeks of 80%.
10 The system, where y = z = 0%, had an RA of 36% after 1 week, and when x = z = 0%, an RA of 1% after 1 week.

	<i>Composition 2:</i> x = 5%	Succinic acid	RA after
15	y = 3.5%		4 weeks:
	z = 0		45%

20 The same composition, but with 5% glycerol instead of succinic acid, had an RA after 4 weeks of 27%.
20 The same composition, but with 5% adipic or glutaric acid instead of succinic acid, had an RA after one week of 40%. (The glutaric acid was added as glutaric acid anhydride).

	<i>Composition 3:</i> x = 2% or 5%	RA after 4 weeks = 100%
25	y = 0	
	z = 8%	

	<i>Composition 4:</i> x = 1%	RA after 4 weeks = 75%
30	y = 0	
	z = 8%	

35 For comparison, the same products but with 2.5 or 5% glycerol instead of succinic acid and 7.5 sodium sulphite:

40	x = 2.5 or 5	
	y = 0	
	z = 7.5	

45 had an RA after 4 weeks of 60%; the same composition but with only 7.5% sulphite:

50	x = 0	
	y = 0	
	z = 7.5	

had an RA of 32% after 1 week.

	<i>Composition 5:</i> x = 5% of saccharic acid	RA after
55	y = 3.5%	8 weeks:
	z = 8%	80%

60 The same composition, but with 5% of glycerol instead of saccharic acid, had an RA after 8 weeks of 80%.

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Composition 6: x = 5% of malonic acid RA after

y = 3.5% 4 weeks:

5 z = 0 44%

Composition 7: x = 5% of maleic acid RA after

10 y = 3.5% 4 weeks:
z = 0 46%

Claims

15 1. An aqueous, enzymatic liquid detergent composition comprising, in an aqueous medium an active detergent material, a detergent builder, enzymes and an enzyme-stabilizing system which contains boric acid, boric oxide or an alkali metal borate, and/or a reducing alkali metal salt having an oxygenated sulphur anion, S_aO_b , in which a and b are whole numbers from 1 to 8, characterized in that the enzyme-stabilizing system further comprises from 0.5—15% by weight of a dicarboxylic acid of the formula
20 $COOH-(CHOH)_a-(CH_2)_b-(CHOH)_c-(CH_2)_d-COOH$, wherein a, b, c and d are whole numbers from 0—4, and the sum of a, b, c and d is from 0 to 4 or of maleic or fumaric acid as well as the alkali metal ammonium alkanolamine or alkaline earth metal salts thereof, or the anhydrides thereof.
25 2. A composition according to claim 1 characterized in that from 2—10% by weight of the dicarboxylic acid is present.
3. A composition according to claim 1, characterized in that the dicarboxylic acid is succinic or saccharic acid.
4. A composition according to claim 3, characterized in that the enzyme-stabilizing agent comprises a mixture of borax, sodium sulphite and succinic acid.

30 4. Patentansprüche

1. Wäßrige enzymhaltige flüssige Detergents-Zusammensetzung umfassend in einem wäßrigen Medium ein aktives Detergents-Material, einen Detergents-Builder, Enzyme und ein Enzym-stabilisierendes System, das Borsäure, Boroxid oder ein Alkalimetallborat und/oder ein reduzierendes Alkalimetallsalz mit einem Sauerstoff-haltigen Schwefelanion S_aO_b in dem a und b ganze Zahlen zwischen 1 und 8 sind, enthält, dadurch gekennzeichnet, daß das Enzymstabilisierende System außerdem 0,5 bis 15 Gew.-% einer Dicarbonsäure der Formel $COOH-(CHOH)_a-(CH_2)_b-(CHOH)_c-(CH_2)_d-COOH$, worin a, b, c und d ganze Zahlen zwischen 0 und 4 sind und die Summe von a, b, c und d zwischen 0 und 4 liegt, oder von Malein- oder Fumarsäure wie auch der Alkalimetall-, Ammonium-, Alkanolamin- oder Erdal-kalimetallsalze davon oder die Anhydride davon umfaßt.
2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß 2—10 Gew.-% der Dicarbonsäure vorhanden sind.
3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Dicarbonsäure Bernsteinsäure oder Zuckersäure ist.
45 4. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß das Enzym-stabilisierende Mittel eine Mischung von Borax, Natriumsulfit und Bernsteinsäure umfaßt.

Revendications

50 1. Composition détergente liquide aqueuse enzymatique comprenant, dans un milieu aqueux, une matière détergente active, un adjuvant de détergence, des enzymes et un système de stabilisation des enzymes qui contient de l'acide borique, l'oxyde borique ou un borate de métal alcalin et/ou un sel réducteur de métal alcalin ayant un anion soufre oxygéné S_aO_b dans lequel a et b sont des nombres entiers de 1 à 8, caractérisée en ce que le système stabilisateur d'enzymes contient en outre de 0,5 à 15% en poids d'un acide dicarboxylique de formule $COOH-(CHOH)_a-(CH_2)_b-(CHOH)_c-(CH_2)_d-COOH$, dans laquelle a, b, c et d sont des nombres entiers de 0 à 4, et la somme de a, b, c et d est de 0, à 4, ou d'acide maléique ou fumrique aussi bien que leurs sels de métaux alcalins, d'ammonium, d'alanol-amines, ou de métaux alcalino-terreux, ou leurs anhydrides.
55 2. Composition selon la revendication 1, caractérisée en ce que l'acide dicarboxylique est présent à raison de 2 à 10% en poids.
3. Composition selon la revendication 1, caractérisée en ce que l'acide dicarboxylique est l'acide succinique ou l'acide saccharique.
60 4. Composition selon la revendication 3, caractérisée en ce que l'agent de stabilisation des enzymes comprend un mélange de borax, de sulfite de sodium et d'acide succinique.
65